

Synthesis Gas Production from CH₄ Reforming with CO₂ over Pd/Al₂O₃ Promoted with CeO₂

Supaporn Therdthianwong ^{*}, Noppon Summaprasit,
Napassorn Junpanichravee,
Apichai Therdthianwong

Chemical Engineering Practice School (ChEPS)
Faculty of Engineering,
King Mongkut's University of Technology Thonburi
91 PrachaUtit Rd. Bangmod, Tungkru, Bangkok 10140, Thailand

(Received : 23 January 2002 – Accepted : 24 July 2002)

Abstract : The reforming of methane with carbon dioxide has been proposed for synthesis gas production for environmental and commercial reasons. In this study the effect of ceria promoter on behavior of Pd/Al₂O₃ in the CO₂ reforming of methane at 600°C was investigated. Ceria loading, calcination temperature of the CeO₂/Al₂O₃ support, and reduction temperature of the catalyst prior to use were assumed to be factors affecting hydrogen yield, H₂/CO ratio and carbon deposited. The promoted catalyst, Pd/CeO₂/Al₂O₃, exhibited

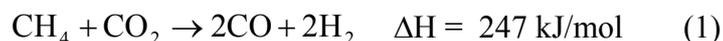
* To whom correspondence should be addressed (email address:
supaporn.the@kmutt.ac.th)

higher stability than the unpromoted catalyst under a normal feed ratio of CH₄/CO₂ (1:1.67) while maintaining good activity. Fifty-hour activity of the catalyst was obtained at an 8% ceria loading and 600°C calcination temperature. Also the H₂/CO ratio in the synthesis gas product was maintained around 1 for 48 hrs on stream. The most suitable reduction temperature was 300°C, since it gave the best catalytic performance. This study supports the observation that the addition of ceria promoter improves Pd/Al₂O₃ catalyst stability. The activity of the regenerated catalyst was also tested. Spent catalyst was regenerated at 650°C but exhibited poor performance compared to fresh catalyst. This could be caused by sintering of Pd atoms at high regeneration temperature resulting in low Pd dispersion.

Keywords: Synthesis gas, Methane, Catalyst, Hydrogen, Ceria promoter.

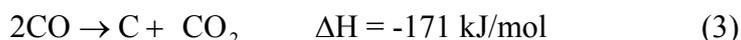
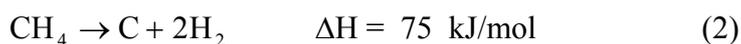
Introduction

Reforming of CH₄ with CO₂ produces synthesis gas with a more suitable H₂/CO ratio than that generated by the widely employed steam reforming reaction. CO₂ reforming has environmental benefits since CO₂, a greenhouse gas, is consumed in reforming while the CO product is used to make alcohol. Sodesawa et al [1] and Edwards and Maitra [2] give good overviews of the chemistry of CO₂ reforming and the current research status of this "dry" reforming reaction:



CO₂ reforming has an important industrial advantage because natural gas normally contains CO₂ as well as C₁ and some higher hydrocarbons. As a result, with dry reforming, natural gas can be fed directly to the reformer unit. The literature describes many applications of dry reforming such as thermo-chemical heat-pipe [1], production of methanol and DME (dimethyl ether), an intermediate for producing synthetic gasoline, and production of an octane enhancer, methyl tertiary butyl ether (MTBE) [3].

Dry reforming is an endothermic reaction carried out in the temperature range of 300-830°C and generally at atmospheric pressure. One of the important problems in dry reforming is coke formation via reaction (2) and (3) which can block the active sites:



Activity and stability of dry reforming catalysts depends strongly on the type of support, the noble metal used and on the presence of a promoter. The literature discusses catalysts such as Ni, Rh [4, 5, 6], Ru [6], Pd [7], Ir and Pt. Stagg and Resasco [8] have made a bimetallic catalyst by adding Sn to Pt. Oxides, both alkaline [9] and rare earth [10, 11], have been used as promoters mainly to prolong the lifetime of the catalysts.

Ceria appears to be a good promoter for palladium on aluminium: it enhances dispersion of the metal and promotes its oxidation to metal oxide [12]. However, ceria loading and calcination temperature of $\text{CeO}_2/\text{Al}_2\text{O}_3$ produced for dry reforming have not been studied. Both of these factors may affect palladium dispersion and thereby the catalyst activity. In addition, the reduction temperature of the catalyst, in the step prior to use when the inactive metal oxide is reduced to form the active metal, is known to have a major influence on catalytic performance of the supported catalyst [13]. Generally, higher reduction temperature provides better metal dispersion [14] up to the point when sintering becomes significant. Satterfield [15] mentions the importance of controlling the reduction temperature. Li, et al [16] have demonstrated that reduction temperature affects the catalytic activity of Pd/CeO_2 .

This research was intended to find suitable ceria loading, calcination temperature and reduction temperature for $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts promoted with CeO_2 in the dry (CO_2) reforming of methane for synthesis gas production. In addition, catalyst regeneration was briefly studied.

Materials, Equipment and Methods

Catalyst Preparation

The CeO₂/Al₂O₃ supports were prepared from cerium nitrate (Ce(NO₃)₂·6H₂O) and aluminium (JRC-ALO-6 supplied by the Catalysts and Chemicals Ind. Co., Ltd. Japan) by deposition method. Palladium precursor was palladium chloride (99.9% PdCl₂) supplied by Sigma. Firstly, ceria was deposited on aluminium by dissolving a specified amount of (Ce(NO₃)₂·6H₂O) in distilled water. Aluminium was added and the solution was stirred for 24 hrs before the liquid was slowly boiled off. The resulting aluminium paste was removed from the beaker and baked in an oven at 110°C for 3 hrs. The support was then calcined in air at 600°C for 4 hrs. For loading Pd, an amount of PdCl₂ calculated to be 1% wt on support was dissolved in HCl with a PdCl₂:HCl ratio of 1:5. The solution was made up to 200 ml by distilled water. Support was added to this palladium solution and stirred for 24 hrs. The excess liquid in the slurry was slowly boiled off. Then the sample was removed from the beaker and baked in an oven at 110°C for 3 hrs and calcined at 350°C for 1 hr. The finished catalyst was stored in a desiccator until use.

Experimental Apparatus

Measurement of catalyst activity for CH₄/CO₂ reforming for all catalyst samples, except those prepared to study the effect of reduction temperature, was conducted at 600°C under atmospheric pressure in a

packed bed reactor made from a 1.27 cm diameter stainless steel 316 tube. The tube was filled with about 0.8 gm of catalyst pellet held in place by quartz wool. The reactor was heated by a temperature-controlled tube furnace. Flow of feed to the reactor was held at 50 ml/min equivalent to a 3,560 cm³/gm-hr space velocity. Gas flow rate was controlled by a Dwyer mass flow controller. For the effect of reduction temperature measurements, the heater used had a shorter heating zone and the amount of catalyst used was about 0.68 gm with the flow of reactant gas 40 ml/min to obtain the same space velocity used for the catalyst activity measurements.

The gas product was collected and analyzed for its composition using a Shimadzu model 9A gas chromatograph equipped with a TCD and Porapak Q and molecular sieve 5A columns. The activity of the catalyst was considered from CH₄ conversion, gas product composition as well as H₂/CO product ratio.

The number of active sites or %Pd dispersion was obtained by dynamic chemisorption using a CHEMBET 3000 unit. The crystal size of ceria was measured using an XRD (X-ray diffractometer).

Experiments Performed

Effect of ceria loading and calcination temperature:

Effect of ceria loading on dispersion of palladium over the Al₂O₃ support and on catalyst activity were studied at a calcination

temperature of 600°C. A loading range from 0-13 wt.% CeO₂ was investigated. Three catalysts promoted with different ceria loadings were chosen for comparison with unpromoted catalyst (0% CeO₂). After these experiments, the effect of calcination temperature of CeO₂/Al₂O₃ at 600, 800 and 1000°C was determined on the samples of ceria loading that exhibited the largest Pd dispersion. Pd dispersion and the number of activated sites were measured by CO pulse chemisorption method using a 0.2 gm catalyst sample that was first calcined in air at 350°C for 1 hr. The remaining moisture or air was removed by passing helium over the sample at 300°C for 2 hrs. The sample was then cooled down to room temperature. Following this it was reduced at 300°C under flowing hydrogen for 2 hrs. Hydrogen remaining in the sample was eliminated by flowing helium over the sample at 300°C for 1 hr. The chemisorption analysis was performed at 35°C using carbon monoxide as adsorbed gas and helium as carrier gas.

For the activity (CH₄/CO₂ reforming) experiments, the catalyst was reduced, *in situ*, at 400°C in a flow of 10% H₂ in N₂ for 2 hrs, followed by an increase in temperature to 600°C under N₂ flow at 22 ml/min. The reaction was initiated by feeding the CH₄:CO₂ (1:1.67) mixture at a flow rate of 50 ml/min. The experiment was performed for ~ 50 hrs, or until the catalyst was deactivated by coke deposition. The amount of coke deposited on spent catalyst was analyzed from the weight change after reaction.

Effect of reduction temperature:

In our study of the effect of reduction temperature, the catalyst was prepared with a ceria loading and used a calcination temperature that showed the highest activity from our first experiments. The CH₄/CO₂ reforming experiment method and condition used for this effect were the same as those in previous experiment, except for the reduction temperature of catalyst. Four catalyst reduction temperatures, 200, 300, 400, and 500°C, were firstly examined by measuring dispersion of palladium and activity in CH₄/CO₂ reforming. An experimental run lasted 3 hrs. Further experimental details and equipment are given elsewhere [17, 18].

Catalyst Regeneration :

In the catalyst regeneration study, the CH₄/CO₂ reforming was performed over the 1%Pd/8%CeO₂/Al₂O₃ reduced at the selected temperature. The operating condition was the same as previously, except that the CH₄:CO₂ was increased to 1:1 to promote coke formation. This is because when CO₂ in the feed decreases, the carbon formed by the dissociation of CH₄ (reaction (2)) [19] does not react with CO₂. The TGA was conducted over the spent catalyst to determine the regenerated temperature at which the carbon was completely burned off. Then the spent catalyst was regenerated in air at the chosen temperature for 1 hr. Thereafter, CH₄/CO₂ reforming was performed over the regenerated catalyst at the normal condition used previously.

Results and Discussion

Effect of Ceria Loading

As found in automotive catalysts [20], ceria is generally added to three-way catalysts to stabilize the aluminium support against coke formation and increase the dispersion of noble metal. The effect of ceria on palladium dispersion of the reforming catalyst investigated by the chemisorption method is shown in Figure 1. The results show that as ceria loading is increased, the palladium dispersion over CeO₂/Al₂O₃ increases up to 2 wt.% ceria. At higher ceria loadings the dispersion decreases until a constant value is reached. Low ceria loading distributed palladium on the support better than high loading, and catalysts promoted with 1-2% CeO₂ had the highest dispersion at ~42%.

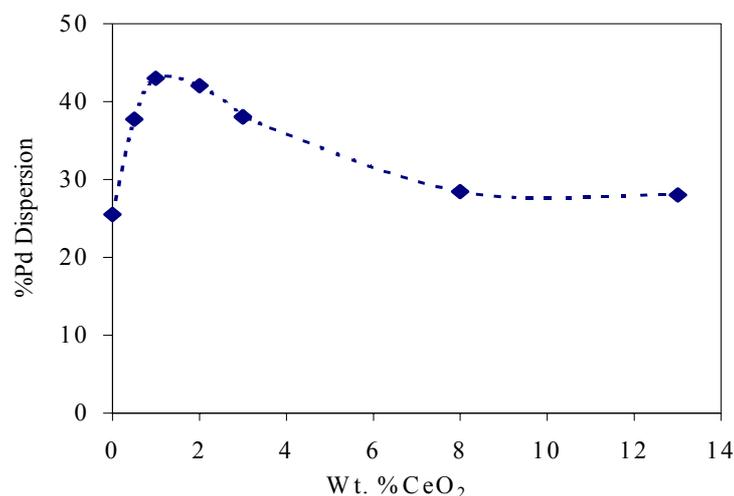


Figure 1. Number of active sites and % Pd dispersion of 1%Pd/Al₂O₃ at various CeO₂ loadings.

To investigate how ceria loading affected the catalyst performance, the promoted catalysts composed of 1%Pd/2%CeO₂/Al₂O₃, 1%Pd/8%CeO₂/Al₂O₃ and 1%Pd/13%CeO₂/Al₂O₃ were used in CH₄/CO₂ reforming. Their activity and stability were compared with the measurements on the unpromoted catalyst (1%Pd/Al₂O₃).

Methane conversion at various times on stream for the four catalysts are illustrated in Figure 2.

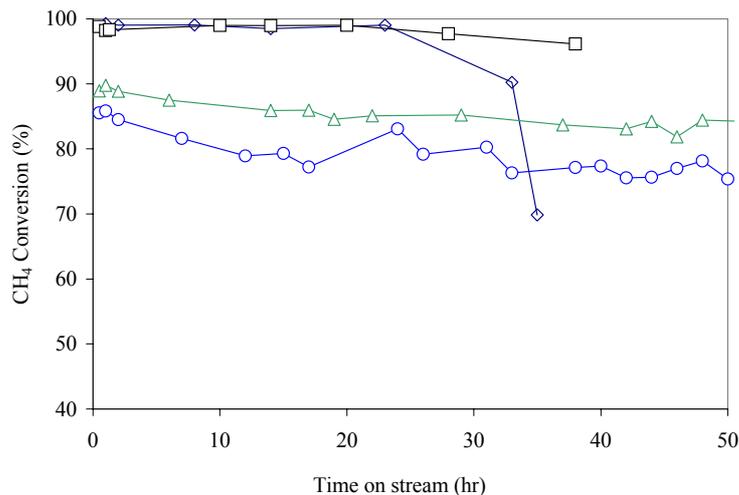


Figure 2. CH₄ conversion of CH₄/CO₂ reforming at 600°C on 1%Pd/Al₂O₃ (◇), 1%Pd/2%CeO₂/Al₂O₃ (□), 1%Pd/8%CeO₂/Al₂O₃ (Δ), 1%Pd/13%CeO₂/Al₂O₃ (○).

The unpromoted catalyst, 1%Pd/Al₂O₃, gave the highest conversion of about 99 %, however its activity decreased gradually until 23 hrs and then rapidly dropped until measurements ceased at 35 hrs after flow blockage through coking took place. For the

1%Pd/2%CeO₂/Al₂O₃ catalyst, the CH₄ conversion was also very high at about 98%. The catalyst coked up after 38 hrs on stream terminating the run. Average conversion for the 1%Pd/8%CeO₂/Al₂O₃ and 1%Pd/13%CeO₂/Al₂O₃ catalyst samples was 82% and 75%, respectively. Activities of these high ceria content catalysts were maintained at these values for 48 hrs without indications of coke blocking. Due to the higher methane conversion and low coke deactivation, the catalyst promoted with 8 wt.% CeO₂ was used for subsequent experiments.

Figure 3 presents the average composition of the gas product over the first 30 hours on stream.

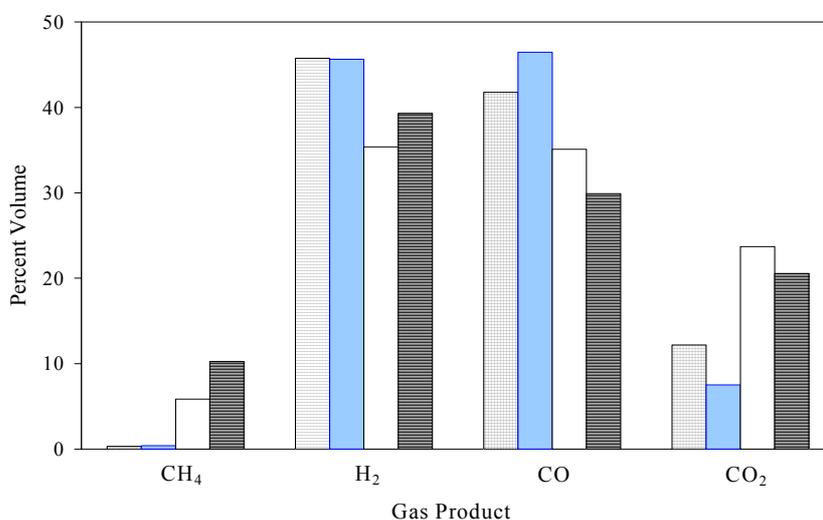


Figure 3. Effect of ceria loading on average gas product composition from CH₄/CO₂ reforming obtained over 1%Pd/Al₂O₃ (▨), 1%Pd/2% CeO₂/Al₂O₃ (■), 1%Pd/8%CeO₂/Al₂O₃ (□) and 1%Pd/13%CeO₂/Al₂O₃ (▩).

Little change in composition occurred during this time. Figure 2 suggests that the 1%Pd/Al₂O₃ and 1%Pd/2%CeO₂/Al₂O₃ catalysts are more active than the others. Nevertheless, the H₂/CO product ratio of all promoted catalysts was found to be around 1 for the first 30 hrs. However, only the 1%Pd/8%CeO₂/Al₂O₃ sample maintained this ratio throughout the experiment as shown in Figure 4.

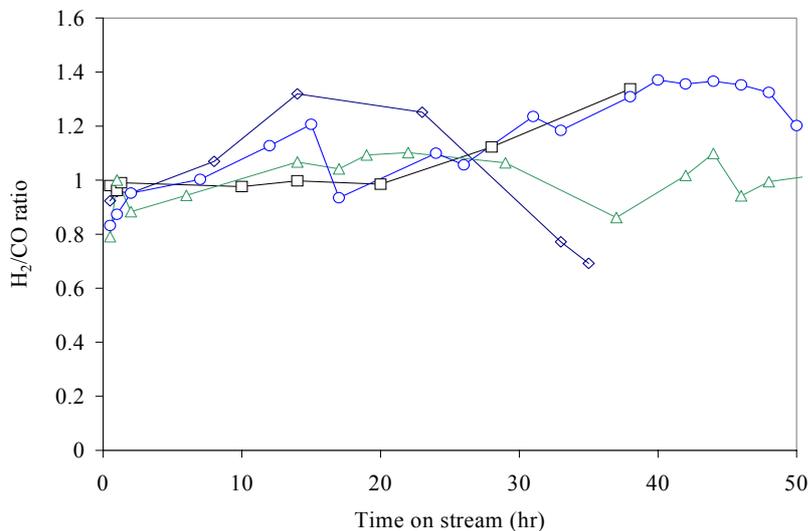


Figure 4. H₂/CO ratio of CH₄/CO₂ reforming at 600°C over 1%Pd/Al₂O₃ (◇), 1%Pd/2%CeO₂/Al₂O₃ (□), 1%Pd/8%CeO₂/Al₂O₃ (△), 1%Pd/13%CeO₂/Al₂O₃ (○).

The 1%Pd/Al₂O₃ catalyst exhibited a H₂/CO product ratio of 1.3, however this decreased rapidly along with CH₄ conversion after 23 hrs of operation. Both decreases can be attributed to the carbon deposition on the metal. Loss of active surface decreased methane

decomposition rate and subsequently the H₂/CO ratio. In contrast, all catalysts promoted with ceria maintained their H₂/CO product ratio for the duration of the measurements. The average H₂/CO ratios in the synthesis gas for the 1%Pd/Al₂O₃ and 1%Pd/2%CeO₂/Al₂O₃ catalysts were about 1.1 and 0.98, respectively. For the 1%Pd/8%CeO₂/Al₂O₃ and 1%Pd/13%CeO₂/Al₂O₃ catalysts, it was 1.0 and 1.2, respectively.

The amount of carbon formed during an experiment was determined by weight change of the catalyst. As the CeO₂ loading increased, the carbon deposition rate (g /g of C in feed) diminished as shown in Figure 5. We believe this is because the ceria promoted catalyst has a self-regenerating mechanism. Richardson [14] suggests

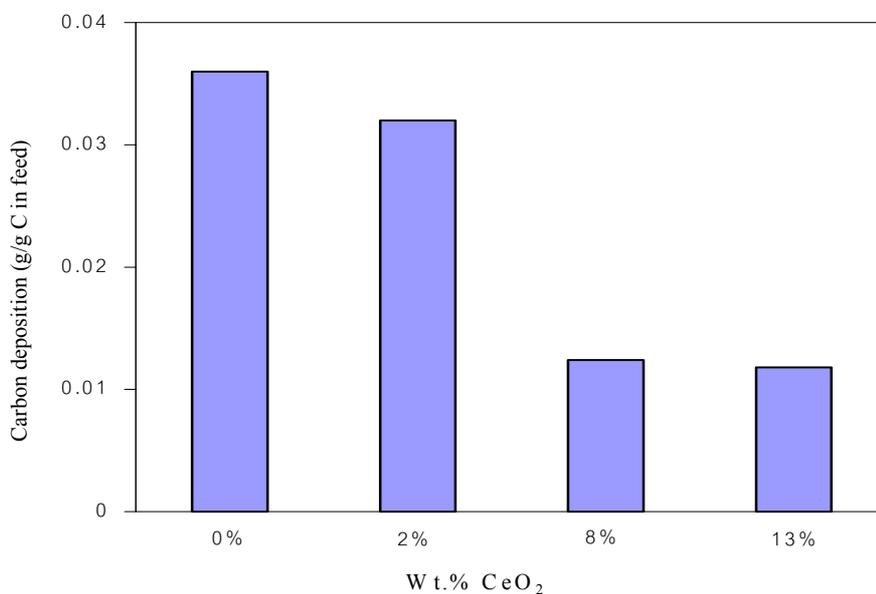


Figure 5. Carbon deposition over 1%Pd/Al₂O₃ catalyst containing different ceria loadings.

that ceria stores oxygen which can react with carbon deposited on Pd to generate CO. Carbon burn-off would arise from surface oxygen species detached from ceria and migrating to Pd (stoichiometric Eqns. 4 and 5 below) or from CO₂ decomposition (Eqn. 6).



Based on these suppositions for the role of ceria in dry reforming, the 1%Pd/8%CeO₂/Al₂O₃ catalyst was chosen to study the effect of calcination and reduction temperature on Pd dispersion and catalyst activity.

Effect of Calcination Temperature

For the same ceria loading, Table 1 shows that an increase in the calcination temperature increased the CeO₂ crystal size. It can be seen also that the 1%Pd/8%CeO₂/Al₂O₃ catalyst calcined at 1000°C and showed the lowest dispersion of Pd compared with samples calcined at 800°C and 600°C. Figure 6 explains how ceria can promote Pd dispersion. Since ceria can adsorb palladium better than the aluminium support [21], as ceria crystal size increases (number of ceria crystals decreases) the palladium agglomeration occurs. The results in Table 1 agree that the sintering of ceria crystal takes place at a temperature of 1000°C. At a temperature lower than 800°C, the

ceria crystal sizes are almost the same, resulting in the similar Pd dispersion.

Table 1. Ceria crystal size, number of active sites and % Pd dispersion for 1%Pd/8%CeO₂/Al₂O₃ catalyst with support calcined at different temperatures.

Calcination temp. (°C)	CeO ₂ Crystal Size (Å)	No. of active sites (molecules/g)	% Pd Dispersion
600	190	1.61×10 ¹⁹	28
800	215	1.47×10 ¹⁹	26
1000	375	8.22×10 ¹⁸	14

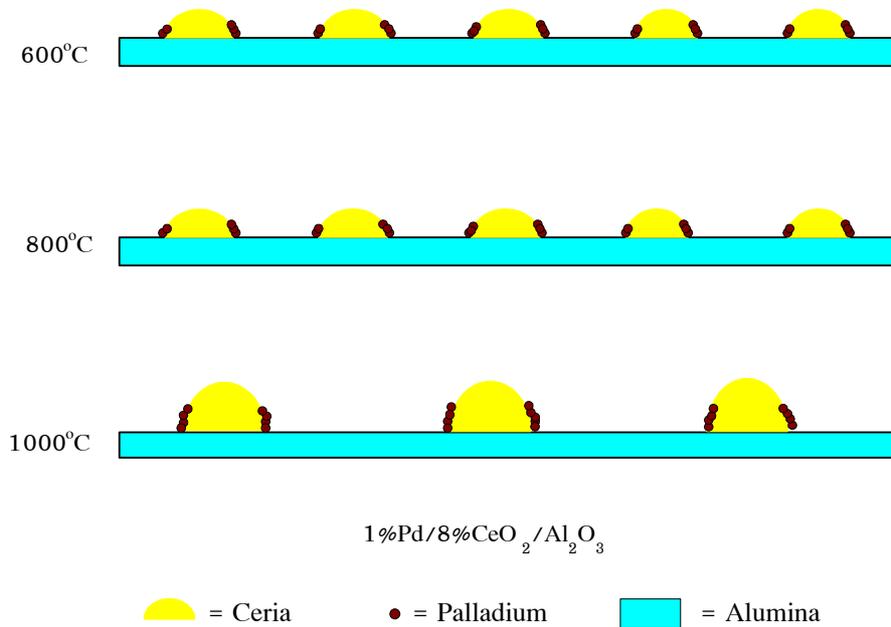


Figure 6. Schematic model of Pd adsorption over CeO₂/Al₂O₃ calcined at different temperatures.

Figure 7 shows the conversion of methane as a function of time on stream for samples of the 8 wt% ceria loading calcined at 600, 800 and 1000°C. Methane conversions in the range of 79%-87% are evident. Loss in conversions were less than 5% over the 50 hr duration of the measurement and all catalysts provided a H₂/CO ratio in the synthesis gas product close to 1.0. Although all catalysts showed similar activity and a similar change with time, higher conversion was obtained when the ceria was loaded.

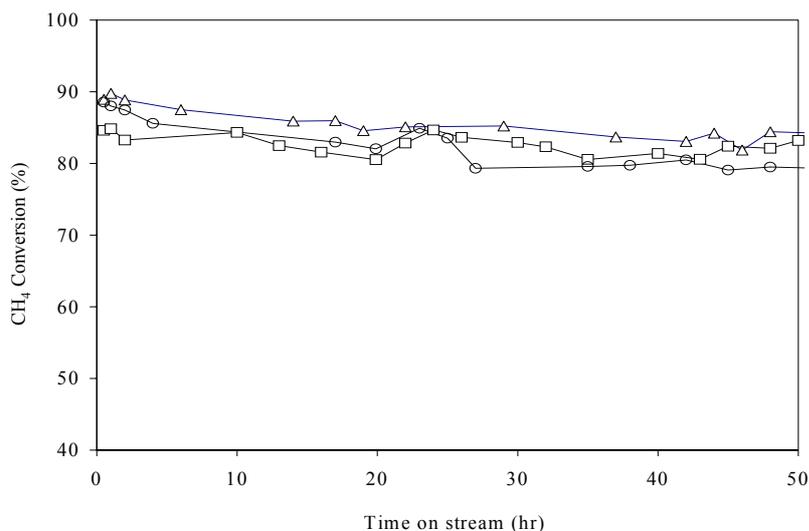


Figure 7. CH₄ conversion of CO₂ reforming reaction over 1%Pd/8%CeO₂/Al₂O₃ at support calcination temperature of 600 °C (Δ) 800 °C (□) and 1000 °C (O).

As the 8 wt%CeO₂/Al₂O₃ support calcined at 600°C gave the best conversion at a satisfactory H₂/CO ratio, this catalyst support was chosen for our study of the effect of reduction temperature.

Effect of Reduction Temperature

Table 2 shows the number of active sites for CO chemisorption and Pd dispersion of catalysts reduced at four different temperatures. As expected, Pd dispersion and the number of active sites increase with reduction temperatures up to 400°C. At 500°C dispersion drops abruptly, probably because at this temperature sintering of Pd metal becomes significant.

Table 2. Number of active sites and Pd dispersion of catalysts reduced at various temperatures.

Reduction temperature (°C)	No. of active sites (molecules/g)	Pd dispersion (%)
200	1.86×10^{19}	33
300	2.41×10^{19}	42
400	2.52×10^{19}	44
500	1.86×10^{19}	33

CH₄ conversion and gas production rate as a function of time on stream are given in Figures 8 and 9 respectively for 4 reduction temperatures of 200 to 500°C. **When the time on stream was more than 1 hr, the activity of most catalysts was reduced. This is because in general the catalyst is initially more active but gradually decreases as time goes by and reaches a steady state if**

no severe deactivation of the catalyst occurs. Reducing the catalyst at 300 °C provides the highest CH₄ conversion and gas production rate over on-stream times up to 3 hrs. The CH₄ conversion obtained from the catalyst reduced at 400°C becomes the same as that obtained from catalyst reduced at 300°C after 2 hrs on stream. In the study of reduction temperature effect, the CH₄ conversions are lower for the cases of reduction temperature at 500 and 200°C. The average CH₄ conversions for 200 to 500°C reduction temperatures are 39%, 71%, 56%, and 49%, respectively. These CH₄/CO₂ reaction results are corresponded with Pd dispersion results.

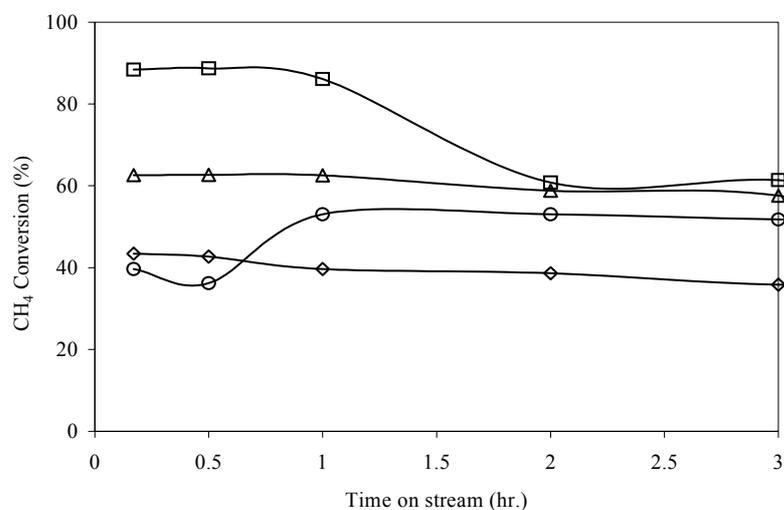


Figure 8. CH₄ conversion for catalysts reduced at different temperatures : T_r = 200°C (◇), T_r = 300°C (□), T_r = 400°C (Δ), T_r = 500°C (O).

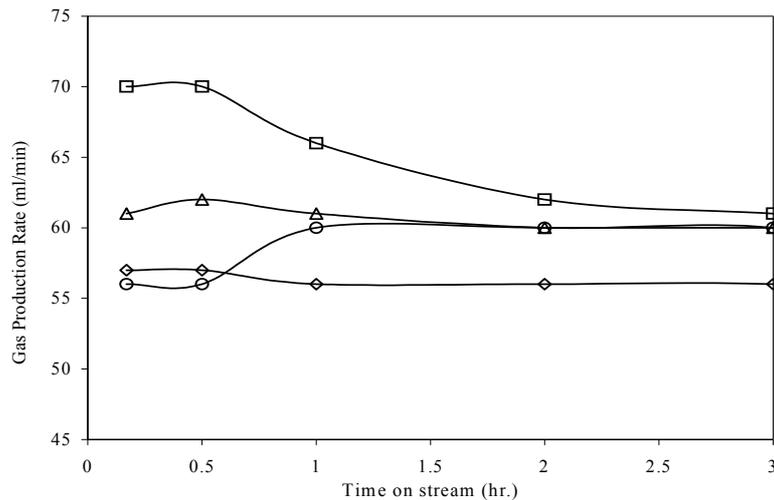


Figure 9. Gas Production rate of catalysts reduced at different temperatures : $T_r = 200^\circ\text{C}$ (◇), $T_r = 300^\circ\text{C}$ (□), $T_r = 400^\circ\text{C}$ (△), $T_r = 500^\circ\text{C}$ (○).

With respect to the H₂/CO ratio, our goal was a value of 1, due to the specific end-use of the synthesis gas. At steady state, the product ratio of catalysts reduced at 300 and 400°C was 0.75, while it was lower for 200°C (0.7) and 500°C (0.5). As confirmed in Figure 3, H₂/CO ratio was initially lower than 1 during the first 5 hrs and started increasing as time on stream increased. A similar result was also observed for 3 hrs experimental time in the reduction temperature study as shown in Figures 8 and 9.

Figure 10 shows the average CH₄ conversion, gas production rate (measured at room temperature and 1 atm. in the unit of ml/min)

and H₂/CO ratio of catalysts reduced at temperatures from 200 to 500°C. The catalyst reduced at 300°C provided the highest CH₄ conversion and gas production rate. Thus for the ranges of ceria and Pd loadings and production conditions investigated, the 1%Pd/8%CeO₂/Al₂O₃ catalyst, reduced prior to use at 300°C with the support calcined at 600°C, appears optimal for CO₂ reforming of methane.

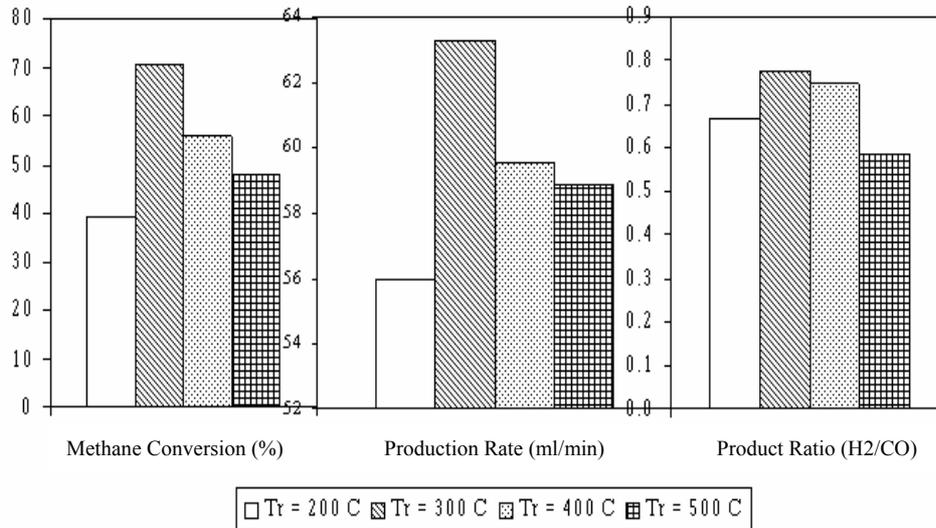


Figure 10. Effect of reduction temperature on catalyst activity in CO₂ reforming.

Investigation of regenerated catalyst activity

After the most suitable reduction temperature was selected, the CH₄/CO₂ reforming was repeated at the same conditions except that the CH₄:CO₂ was increased to 1:1 to promote coke formation. The average value of CH₄ conversion is higher while H₂/CO was lower than those of the 1:1.67 CH₄:CO₂. When sufficient carbon is formed on the catalyst surface, it blocks the active sites and hinders dissociation of CH₄, therefore, CH₄ conversion and H₂ yield decreased when the feed ratio (CH₄:CO₂) increased.

From TGA results of the spent catalyst, 650°C calcination temperature was chosen to regenerate the spent catalyst in air for 4 hrs. The CH₄/CO₂ reforming was then performed over the regenerated catalyst at the conditions previously used (CH₄:CO₂ = 1:1.67). A comparison of catalyst activities between fresh and regenerated catalysts is shown in Figure 11. The catalytic performance of regenerated catalyst was poor compared to that of fresh catalyst, having lower CH₄ conversion, gas production rate and product ratio (H₂/CO). Pd dispersion of the regenerated catalyst reduced at 300 °C was also much lower (8% vs 42%). This was caused by the sintering of Pd at high regeneration temperature (650°C).

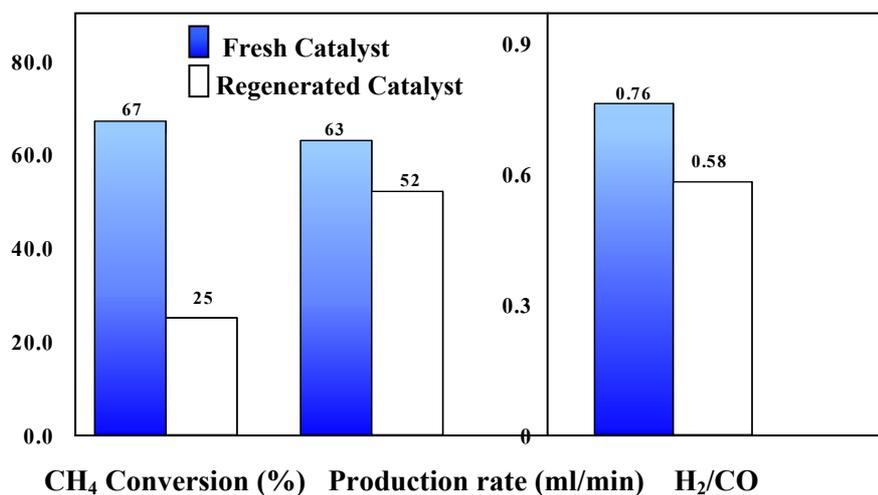


Figure 11. Comparison of catalyst activities between fresh and regenerated catalysts.

This is a preliminary investigation for catalyst regeneration. Further study on this topic is being carried out.

Acknowledgements

The authors gratefully acknowledge financial support for this research from the National Metal and Materials Technology Centre of Thailand (MTEC), NSTDA. Helpful discussions regarding our experiments were held with Professor P.L. Silveston of the University of Waterloo in Canada. Professor Silveston was a visiting expert at KMUTT during the time this manuscript was written.

References

- [1] Sodesawa, T., Dobashi, A., and Nozaki, F. (1979) "Catalytic reaction of methane with carbon dioxide reaction kinetics", *Catalysis Letters*, 12, 107-111.
- [2] Edwards, J.H. and Maitra, A.M. (1995) "The chemistry of methane reforming with carbon dioxide and its current and potential applications", *Fuel Processing Technology*, 42, 269-289.
- [3] Rostrup-Nielsen, J., Dybkjaer, I., Christiansen, L. (1992) *NATO ASI Chemical Reactor Technology for Environmental Safe Reactors and Products*.
- [4] Richardson, J.T. and Paripatyadar, S.A. (1990) "Carbon dioxide reforming of methane with supported Rh", *Appl. Catal.*, 61, 293-309.
- [5] Masai, M, Kado, H., Miyake, A., Nishiyama, S., and Tsuruya, S. (1988) "Methane reforming by carbon dioxide and steam over supported Pd, Pt, and Rh catalysts", *Study of Surface Science Catalysis*, 36, 67-71.
- [6] Perera, J.S.H.Q., Couves, J.W., Sankar, G., Thomas, J.M. (1991) "The catalytic activity of Ru and Ir supported on Eu₂O₃ for the reaction CH₄+CO₂=2H₂+2CO: a viable solar energy system", *Cat. Letters*, 11, 219-225.
- [7] Erdohelyi, A., Csereni, J., Papp, E. and Solymosi, F. (1994) "Catalytic reaction of methane with carbon dioxide over supported palladium", *Appl. Catalysis*, 108, 205-219.

- [8] Stagg, S.M. and Resasco, D.E. (1998) "Effect of promoters on supported Pd catalyst for CO₂ reforming of CH₄", *Surface Science and Catalyst*, 119, 813-818.
- [9] Ruckenstein, E. (1995) "Carbon dioxide reforming of methane over nickel/alkaline earth metal oxide catalysts", *Applied Catalysis*, 133, 149-161.
- [10] Tsipouriari, V.A., Efststhiou, A.M., Zhang, Z.L. and Verykios, X.E. (1994) "Reforming of methane with carbon dioxide to synthesis gas over supported Rh catalysts", *Catalysis Today*, 21, 579-587.
- [11] Cheng, Z., Wu, Q., Li, J. and Zhu, Q. (1996) "Effects of promoters and preparation procedures on reforming of methane with carbon dioxide over Ni/Al₂O₃ catalyst", *Catalysis Today*, 30, 147-155.
- [12] Hegedus, L.L. (Ed.) (1987), *Catalyst Design*, John Wiley & Sons.
- [13] Pinna F. (1998) "Supported metal Catalysts preparation", *Catalysis Today*, 41, 129-137.
- [14] Richardson, T. (1989) *Principles of Catalyst Development*, Texas, Houston, 95-183.
- [15] Satterfield, C.N. (1980) *Heterogeneous Catalysis in Practice*, 2nd ed., New York, McGraw-Hill, 93-107.
- [16] Li F., Fujimoto, and Kaoru (1997) "Comparison of reduction temperature effect on Pd/CeO₂ catalysts in CO or CO₂ hydrogenation", *J. of Graduate School, Faculty of Engineering, University of Tokyo*, 43, 451-466.

- [17] Summaprasit, N. (1999) "Role of ceria promoter on the reforming of methane with carbon dioxide over Pd/Al₂O₃ catalyst", *M.Eng. Thesis*, King Mongkut's Univ. of Tech. Thonburi.
- [18] Jaunpanichravee, N. (1999) "Effect of Reduction Temperature and Regeneration of Pd/CeO₂/Al₂O₃ Catalyst on the CH₄/CO₂ Reforming", *M.Eng. Thesis*, King Mongkut's Univ. of Tech. Thonburi.
- [19] Gustafson, B.L. and Walden, J.V. (1991) "Conversion of CO₂ to CO", *US. Patent*, No. 5,068,057.
- [20] OH, SE H., and Eickel, C.C. (1988) "Effects of Cerium Addition on CO Oxidation kinetics over Alumina-Supported Rhodium Catalysts", *J. of Catalysis*, 112, 543-555.
- [21] Regalbuto, J., and Manarungson, S. (1994) "Adsorption of Noble Metal on CeO₂/Al₂O₃", Paper presented at *AICHE Meeting*, San Francisco, U.S.A.